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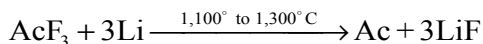
ACTINIUM

[7440-34-8]

Symbol: Ac; a radioactive element; atomic number 89; atomic weight 227.028; electronic config. [Rn]6d¹7s²; oxidation state +3; the principal isotope is ²²⁷Ac, $t_{1/2}$ 21.77 y; emits beta rays forming thorium-227, radium-223 and several short-lived isotopes of radon, polonium, bismuth and lead; a minor isotope is ²²⁸Ac, $t_{1/2}$ 6.15 hr, a beta-emitter producing thorium-228; also several other minor isotopes are known which include: ²²⁵Ac ($t_{1/2}$ 10 ± 0.1 d), ²²⁶Ac ($t_{1/2}$ 1.224 d), ²²⁴Ac ($t_{1/2}$ 2.7 hr), ²²⁹Ac ($t_{1/2}$ 1.04 hr), ²³¹Ac ($t_{1/2}$ 7.5 min), ²³³Ac ($t_{1/2}$ 2.4 min), ²²³Ac ($t_{1/2}$ 2.1 min), ²³⁰Ac ($t_{1/2}$ 2.03 min), and ²³²Ac ($t_{1/2}$ 2.0 min).

Occurrence, Preparation and Uses

Actinium-227 occurs in uranium ore and is a decay product of uranium-235. It is found in equilibrium with its decay products. It is prepared by bombarding radium atoms with neutrons. Chemically, the metal is produced by reducing actinium fluoride with lithium vapor at 1,100°C to 1,300°C.



The element was discovered independently by A. Debierne and F. Giesel in 1899 and 1902, respectively. It is used in nuclear reactors as a source of neutrons.

Physical Properties

Silvery metal; cubic crystal; melts at 1,051°C; vaporizes at 3,198°C; density 10.0 g/cm³

Chemical Reactions

Actinium behaves like lanthanum forming mostly the trivalent salts of the metal. It is strongly electropositive, the first ionization potential being 5.17eV. Reacts with HCl forming AcCl₃; also reacts with organic acids forming corresponding salts; combustion in air can produce oxide and nitride; susceptible to react with CO₂ forming carbonate.

Analysis

The radioactivity can be measured by a beta counter. The metal at trace concentrations can be determined by an atomic absorption or emission spectrophotometer.

Toxicity

Exposure to radiation can cause cancer.

ALUMINUM

[7429-90-5]

Symbol Al; atomic number 13; atomic wt. 26.982; a Group III A (Group 13) metal; principal natural isotope ^{27}Al ; electronic config. $[\text{Ne}]3s^23p^1$; valence +3

Occurrence and Uses

Aluminum is the third most abundant element in the crust of the earth, accounting for 8.13% by weight. It does not occur in free elemental form in nature, but is found in combined forms such as oxides or silicates. It occurs in many minerals including bauxite, cryolite, feldspar and granite. Aluminum alloys have innumerable application; used extensively in electrical transmission lines, coated mirrors, utensils, packages, toys and in construction of aircraft and rockets.

Physical Properties

Silvery-white malleable metal, cubic crystal; melts at 660°C ; b. p. 2520°C ; density 2.70 g/cm^3 ; insoluble in water, soluble in acids and alkalis.

Thermal, Electrochemical, and Thermochemical Properties

Specific heat $0.215\text{ cal/g}\cdot^\circ\text{C}$ ($0.900\text{ J/g}\cdot^\circ\text{C}$); heat capacity $5.81\text{ cal/mol}\cdot^\circ\text{C}$ ($24.3\text{ J/mol}\cdot^\circ\text{C}$); ΔH_{fus} (2.54 kcal/mol (10.6 kJ/mol); ΔH_{vap} 67.9 kcal/mol (284 kJ/mol); E° in aqueous soln. (acidic) at 25°C for the reaction $\text{Al}^{3+} + 3e^- \rightarrow \text{Al}_{(s)}$, -1.66V ; S°_{298} $6.77\text{ cal/degree mol. K}$ ($28.3\text{ J/degree mol.K}$)

Production

Most aluminum is produced from its ore, bauxite, which contains between 40 to 60% alumina either as the trihydrate, gibbsite, or as the monohydrate, boehmite, and diaspore. Bauxite is refined first for the removal of silica and other impurities. It is done by the Bayer process. Ground bauxite is digested with NaOH solution under pressure, which dissolves alumina and silica, forming sodium aluminate and sodium aluminum silicate. Insoluble residues containing most impurities are filtered out. The clear liquor is then allowed to settle and starch is added to precipitate. The residue, so-called "red-mud", is filtered out. After this "desilication," the clear liquor is diluted and cooled. It is then seeded with alumina trihydrate (from a previous run) which promotes hydrolysis of the sodium aluminate to produce trihydrate crystals. The crystals are filtered out, washed, and calcined above $1,100^\circ\text{C}$ to produce anhydrous alumina. The Bayer process, however, is not suitable for extracting bauxite that has high silica content ($>10\%$). In the Alcoa process, which is suitable for highly silicious bauxite, the "red mud" is mixed with limestone and soda ash and calcined at $1,300^\circ\text{C}$. This produces "lime-soda sinter" which is cooled and treated with water. This leaches out water-soluble sodium aluminate, leaving behind calcium silicate and other impurities.

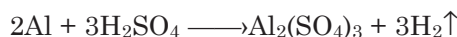
Alumina may be obtained from other minerals, such as nepheline, sodium potassium aluminum silicate, by similar soda lime sintering process.

Metal aluminum is obtained from the pure alumina at 950 to 1000°C electrolysis (Hall-Heroult process). Although the basic process has not changed since its discovery, there have been many modifications. Aluminum is also produced by electrolysis of anhydrous AlCl_3 .

Also, the metal can be obtained by nonelectrolytic reduction processes. In carbothermic process, alumina is heated with carbon in a furnace at 2000 to 2500°C. Similarly, in "Subhalide" process, an Al alloy, Al-Fe-Si-, (obtained by carbothermic reduction of bauxite) is heated at 1250°C with AlCl vapor. This forms the subchloride (AlCl), the vapor of which decomposes when cooled to 800°C.

Chemical Reactions

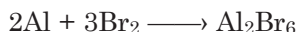
Reacts in moist air forming a coating of Al_2O_3 ; reacts with dilute mineral acids liberating H_2 ,



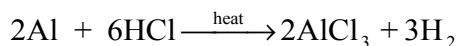
also reacts with steam to form H_2 ; reduces a number of metals that are less active (in activity series), these include Fe, Mn, Cr, Zn, Co, Ni, Cu, Sn, Pb, etc.,



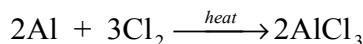
Reactions, e.g., with alkyl halides in ether using Ziegler-Natta catalyst form alkyl aluminum halides, $\text{R}_3\text{Al}_2\text{X}_3$, $[\text{R}_2\text{AlX}]_2$ and $[\text{RAlX}]_2$; with bromine vapor forms anhydrous aluminum bromide,



Combines with iodine vapor forming aluminum iodide, AlI_3 ; heating with HCl gas produces AlCl_3 ,

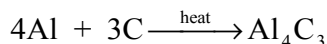


Heating with Cl_2 at 100°C also yields AlCl_3 ,



When the metal is heated with AlCl_3 at 1000°C it forms monovalent aluminum chloride, AlCl .

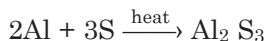
Produces aluminum carbide when the powder metal is heated with carbon at 2000°C or at 1000°C in presence of cryolite,



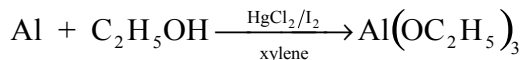
Heating the metal powder over 1000°C with sulfur, phosphorus, or selenium

4 ALUMINUM BROMIDE

forms aluminum sulfide Al_2S_3 , aluminum phosphide, AlP and aluminum selenide, Al_2Se_3 , respectively,



Heating over 1100°C with N_2 produces nitride, AlN; alkoxides are formed when the metal powder is treated with anhydrous alcohol, catalyzed by HgCl_2



Reaction with CO at 1000°C produces the oxide Al_2O_3 and the carbide Al_4C_3 .

Chemical Analysis

The metal may be analyzed by atomic absorption or emission spectrophotometry (at trace levels). Other techniques include X-ray diffraction, neutron activation analysis, and various colorimetric methods. Aluminum digested with nitric acid reacts with pyrocatechol violet or Eriochrome cyanide R dye to form a colored complex, the absorbance of which may be measured by a spectrophotometer at 535 nm.

Hazard

Finely divided aluminum dust is moderately flammable and explodes by heat or contact with strong oxidizing chemicals. Chronic inhalation of the powder can cause aluminosis, a type of pulmonary fibrosis. It is almost non-toxic by ingestion.

ALUMINUM BROMIDE

[7727-15-3]

Formula AlBr_3 ; MW 266.72; Structure: anhydrous AlBr_3 is body-centered crystal, exists in dimeric form as Al_2Br_6 in crystal and also in liquid phases; partially dissociates to monomeric form AlBr_3 in gaseous state; mass spectra show the presence of di-, tetra-, and hexameric forms, Al_2Br_6 , $\text{Al}_4\text{Br}_{12}$, $\text{Al}_6\text{Br}_{18}$, respectively.

Uses

The anhydrous form is used as a catalyst for the Friedel-Crafts alkylation reaction. Its catalytic activity is similar to anhydrous AlCl_3 . Commercial applications, however, are few.

Physical Properties

Colorless crystalline solid in anhydrous form; melts at 97.5°C ; boils at 256°C ;

density 3.01 g/cm³ at 25°C; moisture sensitive, fumes in air; soluble in water (reacts violently in cold water, and decomposes in hot water, alcohols, acetone, hexane, benzene, nitrobenzene, carbon disulfide and many other organic solvents).

Preparation

Prepared from bromine and metallic aluminum.

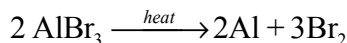


Thermochemical Properties

AlBr_3 (cry)	ΔH_f°	-126.0 kcal/mc
	C_p	24.3 cal/degree
AlBr_3 (gas)	ΔH_f°	-101.6 kcal/mc
AlBr_3 (aq)	ΔH_f°	-214.0 kcal/mc
Al_2Br_6 (gas)	ΔH_f°	-232.0 kcal/mc
AlBr_3 (aq)	S°	-17.8 cal/degree
Al_2Br_6 (gas)	H_{fusion}	10.1 cal/g

Chemical Reactions

Decomposes upon heating in air to bromine and metallic aluminum.



Reacts with carbon tetrachloride at 100°C to form carbon tetrabromide;



Reaction with phosgene yields carbonyl bromide and aluminum chlorobromide;



Reacts violently with water; absorbs moisture forming hexahydrate, $\text{AlBr}_3 \cdot 6\text{H}_2\text{O}$ [7784-27-2]

Chemical Analysis

Elemental composition, Al 10.11% and Br 89.89%; Al analyzed by AA spectrophotometry or colorimetric methods; Br^- analyzed by iodometric titration or ion chromatography and then calculated stoichiometrically; solid may be dissolved in an organic solvent and determined by GC/MS, identified by mass ions $(\text{AlBr}_3)_n$ where n is 2, 4 and 6.

Toxicity

Skin contact can cause tissue burn. It is moderately toxic by all routes of exposure. LD₅₀ oral (rat and mouse): ~1600 mg/kg.

ALUMINUM CHLORIDE

[7446-70-0]

Formula: AlCl_3 ; MW 133.31; Structure and bonding: an electron-deficient compound, a Lewis acid, occurs as dimer Al_2Cl_6 in hexagonal crystal form. Above 300 °C, dissociation to monomer AlCl_3 begins; completely dissociates to AlCl_3 at 1,100°C.

Uses

Aluminum chloride has extensive commercial applications. It is used primarily in the electrolytic production of aluminum. Another major use involves its catalytic applications in many organic reactions, including Friedel-Crafts alkylation, polymerization, isomerization, hydrocracking, oxidation, decarboxylation, and dehydrogenation. It is also used in the production of rare earth chlorides, electroplating of aluminum and in many metal finishing and metallurgical operations.

Physical Properties

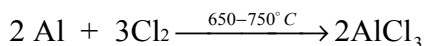
White or light-yellow crystalline solid (or amorphous solid depending on the method of production); odor of HCl; hygroscopic; melts at 190°C at 2.5 atm; sublimes at 181.2°C; density 2.44 g/cm³ at 25°C; decomposes in water evolving heat; soluble in HCl; soluble in many organic solvents, including absolute ethanol, chloroform, carbon tetrachloride and ether; slightly soluble in benzene.

Thermochemical Data

$\Delta H^\circ f(s)$	-168.3 kcal/mol
$\Delta G^\circ f(s)$	-150.3 kcal/mol
S°	26.45 cal/deg mol
$H_{\text{soln.}}$	-77.7 kcal/mol
H_{fus}	8.45 kcal/mol

Preparation

Aluminum chloride is made by chlorination of molten aluminum at temperatures between 650 to 750°C;



or by chlorination of alumina (bauxite or clay) at 800°C in the presence of a reducing agent, such as carbon or CO. It can be prepared by similar high temperature chlorination of bauxite in the presence of a chlorinated organic reductant such as CCl_4 .

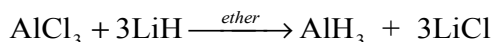
A pelletized mixture of clay, lignite and a small amount of NaCl is chlorinated at 900°C, producing gaseous AlCl_3 (Toth process). Alternatively, alumina is mixed with about 20% by weight carbon and a small amount of sodium

salt. The mixture is chlorinated at 600°C (Bayer process).

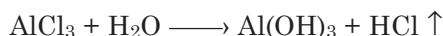
In the laboratory, anhydrous AlCl_3 can be prepared by heating the metal with dry HCl gas at 150°C. The product sublimes and deposits in the cool air condenser. Unreacted HCl is vented out.

Reactions

Reacts with calcium and magnesium hydrides in tetrahydrofuran forming tetrahydro aluminates, $\text{Ca}(\text{AlH}_4)_2$; reacts with hydrides of alkali metals in ether forming aluminum hydride;



Hydrolyzes in chilled, dilute HCl forming aluminum chloride hexahydrate, $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$; reacts violently with water, evolving HCl ,



Hazard

Violent exothermic reactions can occur when mixed with water or alkene. Corrosive to skin.

ALUMINUM CHLORIDE HEXAHYDRATE

[7784-13-6]

Formula: $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$; MW 241.31

Uses

The hexahydrate is used in the preparation of deodorant and antiperspirant. Also, it is applied in textile finishing to improve the antistatic characteristics and flammability ratings of various textile materials. Commercially, it is sold as crystalline powder or as a 28% solution in water.

Physical Properties

White or yellowish deliquescent powder; faint odor of HCl ; density 2.40 g/cm^3 ; soluble in water and polar organic solvents such as alcohol; aqueous solution acidic.

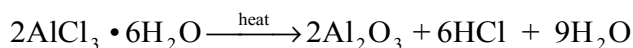
Preparation

Aluminum chloride hexahydrate is prepared by dissolving $\text{Al}(\text{OH})_3$ in conc. HCl and passing gaseous HCl through the solution at 0°C. The precipitate is washed with diethyl ether and dried. Alternatively, it is prepared by hydrolyzing anhydrous AlCl_3 in cold dilute HCl .

8 ALUMINUM HYDRIDE

Reactions

Decomposes to alumina when heated at 300°C;



Reacts with caustic soda solution forming gelatinous precipitate of aluminum hydroxide (hydrrous aluminum oxide); yields aluminum monobasic stearate, $\text{Al}(\text{OH})_2[\text{OOC}(\text{CH}_2)_{16}\text{CH}_3]$ when its solution is mixed with a solution of sodium stearate.

ALUMINUM HYDRIDE

[7784-21-6]

Formula AlH_3 ; MW 30.005; Structure: polymeric, containing residual ether;

Uses

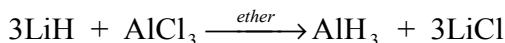
It is used as a reducing agent, and also as a catalyst for polymerization reaction.

Physical and Thermochemical Properties

Colorless cubic crystal; very unstable; decomposes in water; $\Delta H^{\circ}f$ -11.0 kcal/mol (-46.0kJ/mol)

Preparation

Aluminum hydride is prepared by the reaction of lithium hydride with aluminum chloride in diethyl ether



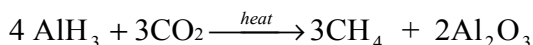
Chemical Reactions

Aluminum hydride decomposes in air and water. Violent reactions occur with both. It forms a complex, aluminum diethyl etherate with diethyl ether. The product decomposes in water releasing heat.

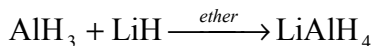


Similar complexes are likely to form with other lower aliphatic ethers. It also forms a 1:1 complex with trimethyl amine, $\text{H}_3\text{Al} \cdot \text{N}(\text{CH}_3)_3$ which reacts explosively with water (Ruff 1967).

Aluminum hydride reduces CO_2 to methane under heating:



Reaction with lithium hydride in ether produces lithium aluminum hydride,



Safety

Many reactions of aluminum hydride or its complexes may proceed with explosive violence, especially with water or moist air.

ALUMINUM NITRATE

[13473-90-0]

Formula: $\text{Al}(\text{NO}_3)_3$; MW 213.00; the anhydrous salt is covalent; also occurs as hydrated salts, $\text{Al}(\text{OH})(\text{NO}_3)_2$, $\text{Al}(\text{OH})_2\text{NO}_3$, and the more stable nonahydrate, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ [7784-27-2]

Uses

The nonahydrate and other hydrated aluminum nitrates have many applications. These salts are used to produce alumina for preparation of insulating papers, in cathode tube heating elements, and on transformer core laminates. The hydrated salts are also used for extraction of actinide elements.

Physical Properties

White or colorless crystalline solid (nonahydrate – rhombic crystal); deliquescent; refractive index 1.54; melts at 73.5°C; decomposes at 150°C; highly soluble in cold water (63.7% at 25°C), decomposes in hot water, soluble in polar organic solvents.

Preparation

The nonahydrate is prepared by treating aluminum, aluminum hydroxide, aluminum oxide, or aluminous mineral with nitric acid. The nitrate is crystallized from the solution.

Reactions

Since $\text{Al}(\text{NO}_3)_3$ or its salt hydrates dissociates to Al^{3+} and NO_3^- ions in the aqueous solution, its reactions in solutions are those of Al^{3+} . It is partially hydrolyzed, producing H_3O^+ and thus accounting for the acidity of its solution in water. The products constitute a complex mixture of mono- and polynuclear hydroxo species.

Aluminum nitrate is soluble in bases, forming aluminates, $[\text{Al}(\text{OH})_4(\text{H}_2\text{O})_2]^-$. It decomposes to Al_2O_3 when heated at elevated temperatures.

Chemical Analysis

Elemental composition: Al 12.67%, N 19.73%, O 67.60%. Al may be analyzed by various instrumental techniques, including atomic absorption or emission spectroscopy, or colorimetry (see under Aluminum). The nitrate anion in aqueous phase may be measured by the NO_3^- ion selective electrode,

ion chromatography, or reduction with cadmium or hydrazine, followed by colorimetric tests.

ALUMINUM NITRIDE

[24304-00-5]

Formula: AlN; MW 40.99

Uses

Aluminum nitride is used in manufacturing of steel and in semiconductors.

Physical Properties

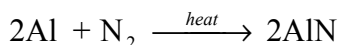
White crystalline solid, hexagonal; odor of ammonia in moist air; sublimes at 2000°C; melts in N₂ atmosphere over 2200°C; density 3.26 g/cm³; decomposes in water, alkalis and acids

Thermochemical Properties

$\Delta H^\circ f(s)$	-76.0 kcal/mol
$\Delta G^\circ f(s)$	-68.6 kcal/mol
S°	4.82 cal/degree mol
C_p	7.20 cal/degree mol

Preparation

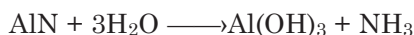
Aluminum nitride may be prepared in the laboratory by heating powdered aluminum metal with nitrogen.



Commercially, it is made by heating an aluminous mineral, such as, bauxite with coal in a stream of nitrogen.

Chemical Reactions

The nitride reacts with water forming aluminum hydroxide and ammonia.



The compound decomposes in alkalis and acids forming products of complex stoichiometry.

Analysis

Elemental composition: Al 65.82%, N 34.18%, the metal is determined by wet analysis or AA spectroscopy. NH₃ liberated on hydrolysis may be determined by titration or colorimetry (see under Ammonia).

ALUMINUM OXIDE

[1344-28-1]

Formula: Al_2O_3 ; MW 101.96; available or prepared in several forms for various commercial applications. Some of these are (i) α -alumina (corundum), (ii) activated aluminas, such as, γ -alumina, η -alumina and ρ -alumina, (iii) hydrated aluminas including aluminum oxide monohydrate, $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ and aluminum oxide trihydrate, $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ (natural gibbsite) and, (iv) acidic, neutral and basic aluminas (no definite chemical compositions; made by adding varying amounts of water to activated aluminas)

Occurrence and Uses

Occurs in nature in abundance; the principal forms are bauxites and laterites. The mineral corundum is used to produce precious gems, such as ruby and sapphire. Activated aluminas are used extensively as adsorbents because of their affinity for water and other polar molecules; and as catalysts because of their large surface area and appropriate pore structure. As adsorbents, they are used for drying gases and liquids; and in adsorption chromatography. Catalytic properties may be attributed to the presence of surface active sites (primarily OH^- , O^{2-} , and Al^{3+} ions). Such catalytic applications include sulfur recovery from H_2S (Claus catalysis); dehydration of alcohols, isomerization of olefins; and as a catalyst support in petroleum refining.

Physical Properties

Al_2O_3	Colorless hexagonal crystal; refractive index 1.768; density 3.965 g/cm ³ (at 25°C); mp 2072°C; bp 2980°C; insoluble in water
$\alpha\text{-Al}_2\text{O}_3$	Colorless rhombic crystal; mp between 2005 to 2025°C; density 4.022 g/m ³ ; hardness 9Moh
$\gamma\text{-Al}_2\text{O}_3$	white microscopic crystal
$\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$	colorless rhombic crystal; refractive index 1.624; density 3.014 g/cm ³
$\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$	white monoclinic crystal; refractive index 1.577; density 2.420 g/cm ³

All forms are insoluble in water.

Thermochemical Properties

$\Delta H^\circ f$	– 400.5 kcal/mol (α-alumina) – 395.0 kcal/mol (γ-alumina crystal) – 390.0 kcal/mol (γ-alumina amorphous) – 472.0 kcal/mol ($\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$) – 612.5 kcal/mol ($\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$)
$\Delta G^\circ f$	– 378.2 kcal/mol (α-alumina) – 436.3 kcal/mol ($\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$) – 546.7 kcal/mol ($\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$)
S°	12.17 cal/deg mol (α-alumina) 3.15 cal/deg mol ($\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ (boehmite)) 16.86 cal/deg mol ($\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ (diaspore)) 33.51 cal/deg mol ($\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ (gibbsite))
C_p	18.89 cal/deg mol (α-alumina) 31.37 cal/deg mol ($\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ (boehmite)) 25.22 cal/deg mol ($\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ (diaspore)) 44.49 cal/deg mol ($\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ (gibbsite))

Preparation

Pure alumina, needed to produce aluminum by the Hall process, is made by the Bayer process. The starting material is bauxite ($\text{Al}_2\text{O}_3 \cdot n\text{H}_2\text{O}$). The ore contains impurities, such as, SiO_2 , Fe_2O_3 , TiO_2 , and Na_2O . Most impurities are removed following treatment with caustic soda solution. Bauxite is dissolved in NaOH solution. Silica, iron oxides and other impurities are filtered out of the solution. CO_2 is then bubbled through this solution. This precipitates out hydrated alumina, which is heated to remove water and produce Al_2O_3 . These impurities are removed. Calcinations of bauxite produce alumina of abrasive and refractory grades. Activated aluminas of amorphous type, as well as the transition aluminas of γ , η , χ , and ρ forms, are obtained from various aluminum hydroxides, such as, α - and β -trihydrates, α -monohydrate and alumina gel. Such chemicals are obtained from bauxite by the Bayer process also.

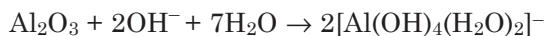
Chemical Reactions

Alumina exhibits amphoteric behavior. It is soluble both in acids and bases. With acids, it produces their corresponding salts. It forms $\text{Al}_2(\text{SO}_4)_3$, $\text{Al}(\text{NO}_3)_3$ and AlCl_3 upon reactions with H_2SO_4 , HNO_3 , and HCl , respectively. In acid medium, it exists as a solvated aluminum ion, in which water molecules are hexacoordinated to trivalent Al^{3+} , as shown below:

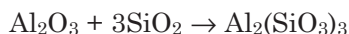


(Rollinson, C. L., 1978., *Aluminum Compounds*. In *Kirk-Othmer Encyclopedia of Chemical Technology*, 3rd ed. Vol 2, pp 188-97. NY,: Wiley Interscience)

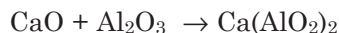
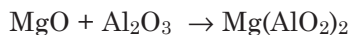
Alumina forms hydroxide in aqueous alkaline solution. The reaction is slow. The products, aluminum hydroxides (hydrated aluminas), contain hexacoordinated aluminohydroxide anion:



In its dry state, alumina exhibiting basicity reacts with silica, forming aluminum silicate



Similarly, with basic CaO or MgO aluminate salts are formed



It forms aluminum nitride, AlN when heated with coal in a stream of nitrogen; and aluminum borate, $\text{Al}_2\text{O}_3 \cdot \text{B}_2\text{O}_3$ when heated with B_2O_3 at 1000°C .

Analysis

Elemental composition: Al 52.91%, O 47.08%. Al may be analyzed by atomic absorption or emission spectrophotometry or by colorimetric methods after acid digestion. Different forms of alumina may be identified by x-ray diffraction analysis. The X-ray crystallographic data for the mineral corundum are as follows:

crystal system:	rhombohedral symmetry
space group	R3c
α_0	4.7591
χ_0	12.9894
z	6
x-ray density	3.9869 g/cm ³

Toxicity

Chronic inhalation of Al₂O₃ dusts may cause lung damage.

ALUMINUM PHOSPHATE

[7784-30-7]

Formula: AlPO₄; MW 121.95

Synonym: Aluminum orthophosphate

Occurrence and Uses

The compound occurs in nature as the mineral, berlinite. Also, it occurs in nature in minerals, amblygonite, [NaAl(PO₄)(OH)]; augelite, [Al₂(PO₄)(OH)₃]; lazulite, [(Mg,Fe)Al₂(PO₄)₂(OH)₂]; variscite [(Al,Fe³⁺)(PO₄)·2H₂O]; and wavelite, [Al₃(OH)₃·(PO₄)₂·5H₂O]. It is used as flux for ceramics; as cement in combination with calcium sulfate and sodium silicate; and in the manufacture of special glasses. It is also used in dried gel and therapeutically as an antacid.

Physical Properties

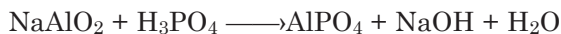
White powdery solid (rhombic plate); the mineral berlinite (AlPO₄) has hexagonal quartz-like structure; refractive index 1.546; mp > 1,500°C; density 2.566 g/cu³; insoluble in water and alcohol; K_{sp} 9.83×10⁻¹⁰ very slightly soluble in HCl or HNO₃.

Thermochemical Properties

$\Delta H^\circ f(s)$	-414.4 kcal/mol
$\Delta G^\circ f(s)$	-368.7 kcal/mol
S°	166.6 cal/degree mol
C _p	22.27 cal/degree mol

Preparation

It is prepared by treating sodium aluminate with phosphoric acid.



It may be prepared by slowly adding (with stirring) ammonium phosphate (0.2*M*) to a solution of aluminum sulfate (0.1*M*).



The compound may, alternatively, be prepared by the reaction of aluminum sulfate with sodium phosphate.



ALUMINUM SULFATE

[10043-01-3]

Formula: $\text{Al}_2(\text{SO}_4)_3$; MW 342.14

Occurrence and Uses

It occurs in nature in minerals; alunite, $\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$ and natroalunite, $\text{NaAl}_3(\text{SO}_4)_2(\text{OH})_6$. The anhydrous salt is used in food applications.

Physical Properties

White powder; refractive index 1.47; density 2.71 g/cm³; mp 770°C (decomposes); hygroscopic; readily soluble in water (31% at 0°C; solubility increases with temperature 98% in boiling water); soluble in dilute mineral acids; slightly soluble in alcohol.

Preparation

The anhydrous salt may be obtained by slow and progressive heating of commercial hydrated salt, $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$. Most water molecules are lost at heating between 250 to 420°C. The last three water molecules are lost between 250 to 420°C at a heating rate of 10°C/min.

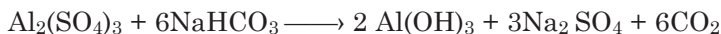
Chemical Reactions

The compound decomposes to γ -alumina and SO_3 when heated between 580 and 900°C. It combines with water forming hydrated salts of various compositions.

Produces calcium aluminate with evolution of SO_3 when calcined with CaCO_3 , (Bayliss, N. S. 1945. *J and Proc. Austral. Chem. Inst.*, 12, 127)



Reacts with NaHCO_3 in aqueous solution, forming fire-extinguishing foams, producing CO_2 , (Albert K. 1937. French Pat. 820,492, November 12, 1937)



Reaction with ammonium phosphate yields AlPO_4 (see Aluminum phosphate, preparation)

Analysis

Elemental analysis: Al 15.77%; O 56.12%; S 28.11%. Al may be determined by colorimetric method or by atomic absorption or emission spectrophotometry; sulfate may be determined by BaCl_2 precipitation method in the aqueous solution of the salt.

ALUMINUM SULFATE OCTADECALHYDRATE

[7784-31-8]

Formula: $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$; MW 648.41

Synonyms: alum, cake alum (the term alum also refers to aqueous solutions of this substance, as well as other hydrate salts containing varying number of waters of crystallization; also the term alum applies to a whole class of sulfate double salts, such as potassium aluminum sulfate or ammonium aluminum sulfate.)

Uses

The compound is used heavily in the paper industry. In its acidic solution form, which contains a slight excess of H_2SO_4 , it is used for pH control of pulp slurries, treatment of process waters, setting of dyes and also for precipitating dissolved resin for setting the size on the fibers. In slight basic form (containing a slight excess of Al_2O_3), it is used for treatment of drinking and waste waters (e.g., for reducing phosphorus content). Other major applications include dyeing, tanning, catalysts, modification of concrete, and in the manufacture of various chemicals and pharmaceutical products.

Physical Properties

White crystal; sweet taste; density 1.62 g/cm³; decomposes at 86.5°C; soluble in water.

Preparation

Prepared from bauxite, kaolin or aluminum compounds on reaction with H_2SO_4 . The insoluble silicic acid is filtered out; the hydrate salt forms on crystallization.

AMERICIUM

[7440-35-9]

Symbol: Am; Atomic Number 95; Atomic Weight 243.0614; an inner-transition, actinide series, radioactive man-made element; electron configuration:

[Rn]⁸⁶ 5*f*⁶6*d*¹7*s*², partially filled *f*-orbitals; valence 2, 3, 4, 5 or 6

Isotopes	Half-life	Decay Mode
Am-237	1.22 hr.	Orbital electron emission
Am-238	1.63 hr.	Orbital electron emission
Am-239	11.90 hr.	Orbital electron emission
Am-240	50.90 hr.	Orbital electron emission Alpha emission
Am-241	432.2 yr.	Alpha emission
Am-242	16.01 hr.	Beta emission (83%) Orbital electron emission (17%)
Am-242	~141 yr.	Isomeric transition (isomer)
Am-243	7,370 yr.	Alpha emission
Am-244	10.1 hr.	Beta emission
Am-244	26 min.	Beta emission (isomer)
Am-245	2.05 hr.	Beta emission
Am-246	39 min.	Beta emission
Am-246	25 min.	Beta emission (isomer)
Am-247	~22 min.	Beta emission

Occurrence

Americium does not occur in nature. It is a man-made element produced in nuclear reactors.

Uses

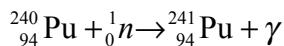
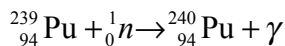
One of its isotopes, Am-241, is a portable source for gamma radiography; also a source of ionization for smoke detectors. In the glass industry, it is used as a radioactive glass thickness gage. Other isotopes do not have much commercial application.

Physical Properties

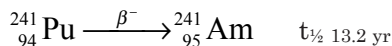
White lustrous metal when freshly prepared; turns silvery; exists in two forms: as a double hexagonal closed-packed alpha form, and a closed-packed cubic structure known as beta form; melts at 994°C; more volatile than its neighbor elements, plutonium or curium; vaporizes at 2,607°C; density 13.67 g/cm³; soluble in dilute acids.

Production

Am-241 may be prepared in a nuclear reactor as a result of successive neutron capture reactions by plutonium isotopes:

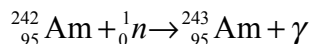
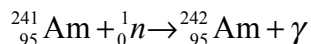


Pu-241 isotope undergoes β -decay forming Am-241:

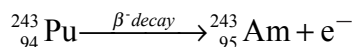
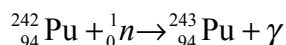
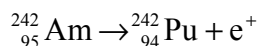
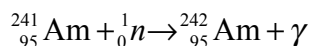


Am-241 obtained as a decay product in the above nuclear reaction (over a peri-

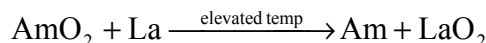
od of years), can be separated by extraction. Am-242 and Am-243 isotopes can be prepared from Am-241 by neutron bombardments:



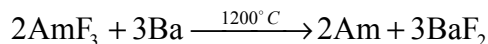
Also, Am-243 can be made from Pu-242, which can be prepared either by very intense neutron irradiation of Pu-239, or from Am-241; resulting from successive neutron-capture reactions.



The Pu-242 obtained in the nuclear reaction is separated by chemical extraction. Americium metal can be prepared from its dioxide by reducing with lanthanum metal at high temperature in a vacuum.



or from its fluoride by reducing the latter with Ba vapors at 1,100°C to 1,200°C:



The metal is soluble in a melt of its trihalide salts.

Americium may be separated from other elements, particularly from the lanthanides or other actinide elements, by techniques involving oxidation, ion exchange and solvent extraction. One oxidation method involves precipitation of the metal in its trivalent state as oxalate (controlled precipitation). Alternatively, it may be separated by precipitating out lanthanide elements as fluorosilicates leaving americium in the solution. Americium may also be oxidized from trivalent to pentavalent state by hypochlorite in potassium carbonate solution. The product potassium americium (V) carbonate precipitates out. Curium and rare earth metals remain in the solution. An alternative approach is to oxidize Am^{3+} to AmO_2^{2+} in dilute acid using peroxydisulfate. AmO_2^{2+} is soluble in fluoride solution, while trivalent curium and lanthanides are insoluble.

Ion exchange techniques have been widely applied in the separation process. In the large-scale ammonium thiocyanate process, the metal is retained on strong base anion exchanger; thus, separating it from the lighter lanthanide elements which are not strongly absorbed on the resin.

Americium and other actinide elements may be separated from lanthanides by solvent extraction. Lithium chloride solution and an eight to nine carbon tertiary amine are used in the process. Americium is then separated from curium by the above methods.

Chemical Reactions

The metal forms its oxide, AmO on its surface in contact with air or oxygen. Similarly, reaction with hydrogen forms the hydride, AmH_2 .

Divalent Am^{2+} is less stable than the corresponding divalent lanthanide elements. It has not been found in aqueous solutions, even after treatment with strong reducing agents.

Am^{3+} is the most stable oxidation state of the metal. In trivalent state, its properties are similar to europium. Am^{3+} reacts with soluble fluoride, hydroxide, phosphate, oxalate, iodate and sulfate of many metals forming precipitates of these anions; e.g., $\text{Am}(\text{OH})_3$, $\text{Am}(\text{IO}_3)_3$, etc.

No stable divalent salt is known. However, Am^{2+} has been detected in CaF_2 matrix (0.1% Am) by paramagnetic resonance spectrum at low temperature. Its formation is attributed to the reduction of Am^{3+} by electrons in the lattice set free by the effects of alpha particle emission.

Trivalent Am^{3+} ions occur in aqueous acid solution. The solution has a pink color and the ion exists as a hydrated species. Reactions with halide salts or the acids produce trihalides.

In solution Am^{4+} ion is not so stable, slowly reducing to trivalent Am^{3+} . However, simple and also complex tetravalent compounds of americium are known. Some examples are $\text{Am}(\text{OH})_4$, AmF_4 , LiAmF_8 , and K_2AmF_4 . $\text{Am}(\text{OH})_4$ is stable in basic solution and results from the oxidation of $\text{Am}(\text{OH})_3$ by hypochlorite ion.

All pentavalent americium compounds are complex salts. Examples are KAmO_2CO_3 , KAmO_2F_2 and Li_3AmO_4 . These are formed upon oxidation of Am^{3+} . For example, Am^{3+} reacts with hypochlorite ion in hot K_2CO_3 , precipitating KAmO_2CO_3 as a crystalline solid.

No simple hexavalent americium compound is known. All Am^{6+} compounds are complex salts containing oxygen. Examples are Li_6AmO_6 , $\text{NaAmO}_2\text{Ac}_3$ (Ac is acetate ion), AmO_2F_2 and Ba_3AmO_6 . Hexavalent americium ion is a strong oxidizing agent and is reduced to AmO^{+2} in oxidation-reduction reactions. Am ion in higher oxidation states is reduced to Am^{3+} by Am-241 alpha radiation.

Safety Precautions

Am emits alpha and gamma radiation. The alpha decay of the isotope Am-241 is three times as active as radium and is associated with 59 KeV gamma radiation, which is a serious health hazard. The alpha energies of Am-241 and Am-243, the two longest lived isotopes, are 5.48 and 5.27 MeV, respectively, accompanied with gamma rays. Therefore, a totally enclosed storage system using x-ray glass should be used, maintaining a slight negative pressure.

AMMONIA

[7664-41-7]

Formula; NH_3 ; MW 17.03; tetrahedral planar geometry, $\text{H}-\text{N}-\text{H}$ bond angle 107.3° ; $\text{N}-\text{H}$ bond distance $1.016\text{\AA}$; dipole moment of the gas 1.46×10^{-18} esu; a Lewis base.

Occurrence and Uses

Ammonia occurs in nature, being constantly formed by putrefaction of the protein of dead animals and plants. While some of it is washed away by the rain into rivers and oceans where it is recycled and converted into proteins by microorganisms, much of it is rapidly absorbed from the earth by living plants making new proteins. Ammonia occurs in urine from which it was produced earlier by chemists and alchemists for use as a soluble base. It occurs in gas liquor obtained from coal gas and producer gas plants and coke ovens. Gas liquor was a major source for producing ammonia before Haber-Bosch process was developed. Combustion of coal, fuel oil, wood and natural gas, as well as forest fires produce ammonia in small amounts in the range 1 to 10 lb per ton. It occurs in many industrial effluents, wastewaters, and groundwaters at trace concentrations. It is also found at trace levels in varying concentrations in the air in most metropolitan cities.

The single largest use of ammonia is its direct application as fertilizer, and in the manufacture of ammonium fertilizers that have increased world food production dramatically. Such ammonia-based fertilizers are now the primary source of nitrogen in farm soils. Ammonia also is used in the manufacture of nitric acid, synthetic fibers, plastics, explosives and miscellaneous ammonium salts. Liquid ammonia is used as a solvent for many inorganic reactions in non-aqueous phase. Other applications include synthesis of amines and imines; as a fluid for supercritical fluid extraction and chromatography; and as a reference standard in ^{15}N -NMR.

Physical Properties

Colorless gas; pungent suffocating odor; human odor perception 0.5 mg/m^3 ; liquefies by compression at 9.8 atm at 25°C , or without compression at -33.35°C (at 1 atm); solidifies at -77.7°C ; critical temperature and pressure, 133°C and 112.5 atm, respectively; vapor density 0.59 (air=1); density of liquid ammonia 0.677 g/mL at -34°C ; dielectric constant at -34°C is about 22; extremely soluble in water; solution alkaline; pK_a 9.25 in dilute aqueous solution at 25°C ; the gas does not support ordinary combustion, but burns with a yellow flame when mixed in air at 16–27% composition.

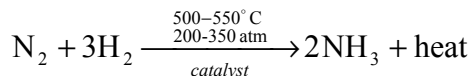
Thermochemical Properties

$\Delta H^\circ f$ (g)	−11.02 kcal/mol
$\Delta H^\circ f$ (aq)	−19.19 kcal/mol
$\Delta H^\circ f$ [$\text{NH}_4^+(\text{aq})$]	−31.67 kcal/mol
$\Delta G^\circ f$ (g)	−3.94 kcal/mol

$G^\circ f$ (aq)	-6.35 kcal/mol
$\Delta G^\circ f$ [NH ₄ ⁺ (aq)]	-18.97 kcal/mol
S° (g)	45.97 cal/degree mol
S° (aq)	26.6 cal/degree mol
S° [NH ₄ ⁺ (aq)]	27.1 cal/degree mol
C_p° (g)	8.38 cal/degree mol
C_p° [NH ₄ ⁺ (aq)]	19.1 cal/degree mol
ΔH_{vap}	5.57 kcal/mol

Synthesis

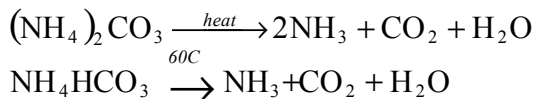
Ammonia is produced from nitrogen and hydrogen at elevated temperature (500 to 550°C) and pressure (200–350 atm) (Haber–Bosch process), using a promoted iron catalyst



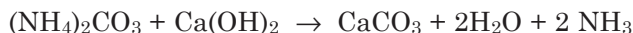
In the above process, finely divided iron oxide combined with sodium oxide and silica or alumina is used as the catalyst. The reaction is favored (as per Le Chatelier's principle) by high pressure and low temperature. However, a temperature of 500 to 550°C is employed to enhance the reaction rate and prevent catalyst deactivation. Although at 200°C and 250 atm the equilibrium may yield up to 90% ammonia, the product yield is too slow. The sources of hydrogen in commercial processes include natural gas, refinery gas, water gas, coal gas, water (electrolysis) and fuel oil, and the nitrogen source is liquefied air.

Most other synthetic processes are modifications of the Haber–Bosch process, using different pressures, temperatures, gas velocities, and catalysts.

Ammonia may be obtained by decomposition of ammonium carbonate or bicarbonate. Such reactions, however, are not applied in commercial production.



Ammonia also may be produced as a by-product from gas liquor obtained from coal, gas, and coke ovens. Organic nitrogen in the coal converts to ammonium compounds which are separated from tar and distilled with an aqueous suspension of Ca(OH)₂ to produce ammonia.



Reactions

Ammonia is stable at ordinary temperatures but begins to decompose to H₂ and N₂ at 450°C. Decomposition is catalyzed by porcelain, pumice and metal

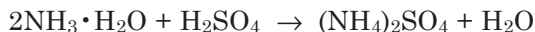
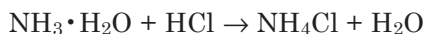
surfaces (but not glass) in presence of which the dissociation starts at 300°C and completes around 500 to 600°C.

Ammonia reacts with water producing NH_4OH . The reaction is reversible; NH_4OH dissociates into NH_4^+ and OH^- ions in solution;

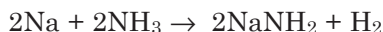


NH_4OH is probably unstable in the molecular form, dissociating into ions. There is evidence of existence of $\text{NH}_3 \cdot \text{H}_2\text{O}$ and $2\text{NH}_3 \cdot \text{H}_2\text{O}$ species in aqueous solution (J.R. LeBlanc, (Jr), Madhavan, S. and R.E. Porter. 1978. Ammonia. In *Kirk-Othmer Encyclopedia of Chemical Technology*, 3rd ed., Vol. 2 p. 474, New York: Wiley Interscience). Formation of such adducts may be attributed to hydrogen bonding.

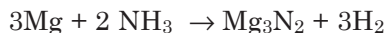
Gaseous NH_3 and its aqueous solution is weakly basic, undergoing neutralization reactions with acids. It reacts with HCl , H_2SO_4 , HNO_3 to form corresponding ammonium salts (after the loss of water from evaporation):



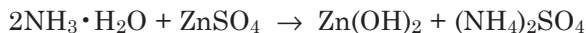
Similar neutralization reactions occur with phosphoric, acetic and other acids. Liquid ammonia reacts with alkali metals forming amides and liberating H_2 . The reaction occurs in presence of a catalyst (e.g., Pt black). Alternatively, heating alkali metals in a stream of ammonia yields their amides.



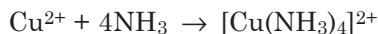
Reacts with Mg to form magnesium nitride, Mg_3N_2 liberating H_2 :



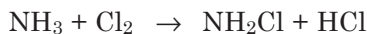
Aqueous ammonia reacts with solutions of many metal salts forming precipitates of metal hydroxides:

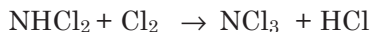
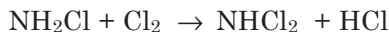


Forms cupric hydroxide, $\text{Cu}(\text{OH})_2$ with CuSO_4 ; the precipitate, however, dissolves in excess ammonia, forming a tetrammine copper (II) complex ion.



Reacts with chlorine forming chloramines: monochloramine, dichloramine and nitrogen trichloride:

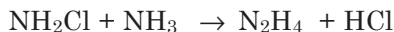




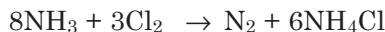
Such chloramines may occur in trace quantities in many chlorine-treated wastewaters that also contain trace ammonia. NCl_3 combines with ammonia to form an unstable adduct, $\text{NCl}_3 \cdot \text{NH}_3$ which reacts with excess NH_3 producing NH_4Cl and liberating N_2 .



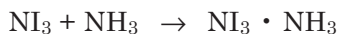
Chloramine is also formed when chlorine is passed into liquid ammonia; further reaction with ammonia produces hydrazine:



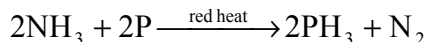
However, with excess ammonia, chlorine and bromine form ammonium chloride and bromide, respectively, liberating N_2 :



Reaction with hypochlorite solution also produces chloramine. Ammonia reacts with iodine to form nitrogen triiodide, which further combines with a molecule of NH_3 to form an adduct $\text{NI}_3 \cdot \text{NH}_3$, an insoluble brown-black solid which decomposes upon exposure to light in the presence of NH_3 :



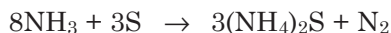
Reacts with carbon at red heat to give ammonium cyanide, NH_4CN ; forms phosphine and nitrogen upon reaction with phosphorus vapor at red heat:



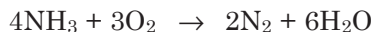
Liquid ammonia reacts with sulfur forming nitrogen sulfide and H_2S :



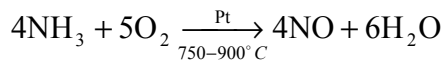
whereas gaseous ammonia and sulfur vapor react to form ammonium sulfide and N_2 :



Heating with oxygen or air produces nitrogen and water:



However, reaction at 750°C to 900°C in presence of platinum or platinum-rhodium catalyst produces nitric oxide and water:

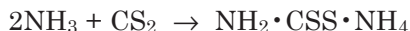
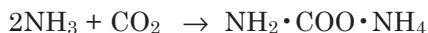


Reacts with oxides of copper, zinc, silver and many metals other than those of Group 1A and Mg at high temperatures, decomposing to N₂ and water. At ambient temperatures strong oxidants oxidize ammonia:



Reactions with H₂S at different stoichiometric ratios may produce ammonium sulfide, hydrosulfide, NH₄HS and polysulfide (NH₄)₂S₃ having varying S contents, depending on temperature and stoichiometric ratios.

Forms ammonium carbamate, NH₂•COO•NH₄ with CO₂ and ammonium dithiocarbamate, NH₂•CSS•NH₄ with CS₂:



The carbamate decomposes to urea and water when heated. Reaction with chromic acid forms ammonium dichromate, (NH₄)₂Cr₂O₇:



Reactions with organic acids such as formic, acetic, benzoic, oxalic, and salicylic acids produce their corresponding ammonium salts; concentrated ammonia solution in excess forms ammonium stearate, CH₃•(CH₂)₁₆•COONH₄ with stearic acid.

Forms a red-colored double salt, ammonium ferric chromate, NH₄Fe(CrO₄)₂ when added to an aqueous solution of Fe(NO₃)₃•6H₂O and CrO₃.

Forms a number of coordination compounds (ammonia complex) with several metals; adds to AgCl forming soluble complex [Ag(NH₃)₂]Cl; forms tetraamine complex [Cu(NH₃)₄]SO₄ with CuSO₄; and forms many hexamine complexes with cobalt, chromium, palladium, platinum and other metals.

Ammonia undergoes “ammonolysis” reactions with many classes of organics including alcohols, ketones, aldehydes, phenols, and halogenated hydrocarbons. Addition and substitution reactions of ammonia are utilized in many organic syntheses. Reactions of liquid ammonia with ethanol, or gaseous ammonia with ethyl iodide, produce diethylamine, monoethylamine, and triethylamine in lesser amounts. Many organic amines and imines are synthesized using ammonia. For example, reaction with ethylene dichloride gives ethylenediamine.

Analysis

Ammonia may be readily identified from its odor. It may be measured by titrimetry. It is absorbed in an excess amount of a standard solution of dilute sulfuric acid and the excess unreacted acid is back titrated against a standard solution of caustic soda using methyl orange indicator. Alternatively, potentiometric titration may be used to find the end point. Concentrations at trace levels in wastewaters, groundwaters, drinking waters, and air may be measured by various colorimetric techniques or by the ammonia-selective electrode method (APHA, AWWA and WEF, 1999. *Standard Methods for the Examination of Water and Wastewater*, 20th ed. Washington, DC, American Public Health Association). Ammonia reacts with Nessler reagent under alkaline conditions, forming a yellow color. The intensity of color is measured by spectrophotometer, absorbance being proportional to concentration of ammonia in the solution. Alternatively, it may be analyzed by the indophenol blue method. Ammonia reacts with hypochlorite to form monochloramine which reacts with phenol in the presence of manganous sulfate catalyst to produce blue indophenol (Patnaik, P. 1997. *Handbook of Environmental Analysis*. Boca Raton, FL, Lewis Publishers). Solutions at high concentrations may be appropriately diluted to measure ammonia within the calibration range in colorimetric and electrode methods.

Hazard

Ammonia causes intense irritation of eyes, nose and respiratory tract which can lead to tears, respiratory distress, chest pain, and pulmonary edema. A few minutes exposure to 3,000 ppm can cause severe blistering of skin, lung edema, and asphyxia which can lead to death (Patnaik, P. 1992. *A Comprehensive Guide to the Hazardous Properties of Chemical Substances*, p. 304. New York, Van Nostrand Reinhold). Contact with liquid ammonia can cause serious blistering and destruction of skin tissues. LC₅₀ inhalation (mouse): 4,200 ppm/hr.

Fire or explosion hazard may arise from the following ammonia reactions: Reaction with halogens produces nitrogen trihalides which explode on heating; its mixture with fluorine bursts into flame; reacts with gold, silver, or mercury to form unstable fulminate-type shock-sensitive compounds; similarly, shock-sensitive nitrides are formed when ammonia reacts with sulfur or certain metal chlorides, such as mercuric, or silver chloride; liquid ammonia reacts violently with alkali metal chlorates and ferricyanides.

AMMONIUM ACETATE

[631-61-8]

Formula: CH₃COONH₄; MW 77.08

Uses

Ammonium acetate is used for preserving meats; as a mordant in the dyeing of wool; in analytical chemistry for standardization of electrodes, and in titra-

tions; also as a therapeutic diuretic and diaphoretic.

Physical Properties

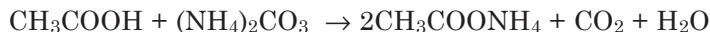
White crystalline solid; deliquescent; melts at 114°C; decomposes at elevated temperatures; density 1.17 g/cm³ at 20°C, density of a 10% solution 1.022 g/mL, and a 50% solution 1.092 g/mL; very soluble in cold water (1,480 g/L at 4°C); also soluble in cold alcohol and acetone (78.9 g/L in methanol at 15°C); solution loses ammonia on standing and becomes acidic.

Preparation

Ammonium acetate is made by exact neutralization of acetic acid with ammonia to neutral pH (pH 7):

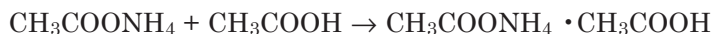


Instead of aqueous solutions, hot glacial acetic acid and anhydrous ammonia may be used. Ammonium acetate also is prepared by reaction of acetic acid with ammonium carbonate:



Reactions

Ammonium acetate forms an acid salt, ammonium acetate double salt, with hot acetic acid:



The acid salt readily dissolves in water and melts at 66°C.

Water-insoluble lead iodide dissolves in ammonium acetate solution, lead acetate and ammonium iodide are formed:



AMMONIUM BICARBONATE

[1066–33–7]

Formula: NH_4HCO_3 ; MW 79.06

Synonyms: ammonium hydrogen carbonate; ammonium acid carbonate

Uses

Ammonium bicarbonate is used in preparing baking dough; in the production of ammonium salts; in heat-exchanger tubes as a scale-removing compound; in fire-extinguishing compositions; in cooling baths; in the manufacture of porous plastics and ceramics; and as a “smelling salt,” mixed with oil of lavender.

Physical Properties

White crystalline solid; prismatic crystal; faint odor of ammonia; stable at ambient temperature but decomposes on heating at 60°C; melts at 107.5°C on very rapid heating; density 1.586 g/cm³; vapor pressure 435 torr at 25°C; readily dissolves in water (21.6g/100g at 20°C, and 36.6g/100g at 40°C).

Manufacture

Ammonium bicarbonate is made by passing carbon dioxide through an aqueous solution of ammonia in an absorption column or a packed tower:



In this process, ammonia solution flows countercurrent to the ascending stream of CO₂. Crystals of ammonium bicarbonate precipitate out when the solution becomes sufficiently saturated. The crystals are filtered or centrifuged out of the mother liquor, washed, and air-dried. Pure product may be obtained by using high purity CO₂. Alternatively, high purity ammonium bicarbonate may be obtained by subliming the product formed at relatively low temperatures.

Reactions

Ammonium bicarbonate decomposes to CO₂, ammonia, and water vapor on heating; it liberates CO₂ when treated with dilute mineral acids:



It reacts with sulfates of alkaline-earth metals precipitating out their carbonates:



The above reaction is applied in descaling calcium sulfate scale in heat-exchanger tubes.

Ammonium bicarbonate forms double salts with many other salts.

AMMONIUM BIFLUORIDE

[1341–49–7]

Formula: NH₄HF₂; MW 57.04

Synonym: ammonium hydrogen fluoride

Uses

NH₄HF₂ is used to solubilize silica and silicates in siliceous rocks of oil wells, thus to regenerate oil flow; as a neutralizer for alkalis in textile plants and commercial laundries; for removing stains from fabrics; for treating, polishing and rapid frosting of glass plates, window panes, picture frames, ampoules and optical lenses; to produce pure salts of metal fluorides; in treat-

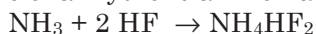
ment processes to prevent corrosion on magnesium and its alloys; in the preservation of wood; and in aluminum anodizing formulations.

Physical Properties

Orthorhombic or tetragonal crystals; etches glass; deliquescent; density 1.50 g/cm³; refractive index 1.390; melts at 125.6°C; very soluble in water; slightly soluble in alcohol.

Preparation

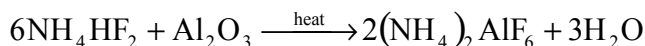
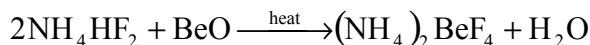
Commercial grade salt containing 1% NH₄F is made by gas-phase reaction of one mole of anhydrous ammonia with two moles of hydrogen fluoride:



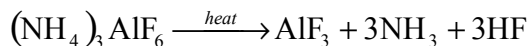
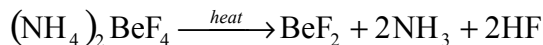
It may also be prepared in the anhydrous form by dehydration of ammonium fluoride solution, followed by thermal decomposition of dry crystals.

Reactions

Thermal dissociation produces ammonium fluoride and ammonia; at elevated temperatures products contain ammonia and hydrogen fluoride. It forms a colorless double salt, ammonium iron fluoride 3NH₄F • FeF₃, with iron, a reaction of commercial application for removing stains from fabric. It reacts with many metal oxides at elevated temperatures forming double fluorides:

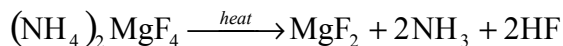
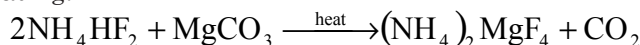


On further heating, the double fluorides decompose to metal fluorides, liberating ammonia and hydrogen fluoride:



The above reactions are employed commercially for obtaining metal fluorides in high purity.

Similar reactions occur with many metal carbonates at elevated temperatures, producing double fluorides. The latter decompose to metal fluorides on further heating:



Analysis

Elemental composition: F 66.61%; H 8.83%; N 24.55%

A measured amount of salt is thermally decomposed to ammonia and hydrogen fluoride. These gases liberated in stoichiometric amounts are

absorbed in excess standard sulfuric acid solution. Ammonia is measured by back titration of excess acid against a standard solution of caustic soda, using methyl orange indicator. Fluoride ion is measured with an ion-specific electrode. Ammonia may be collected and measured by alternative techniques (see Ammonia).

AMMONIUM BROMIDE

[12124–97–0]

Formula: NH_4Br ; MW 97.94; ionic salt, cubic crystal

Uses

Ammonium bromide is used for photography in films, plates, and papers; in fireproofing of wood; in lithography and process engraving; in corrosion inhibitors; and in pharmaceutical preparations.

Physical Properties

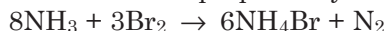
White crystal or granule; strong saline taste; no odor; slightly hygroscopic; density 2.429 g/cm^3 at 25°C ; refractive index 1.712; sublimes at elevated temperatures: vapor pressure 54.75 torr at 300°C and 758.2 torr at 395°C ; highly soluble in water: 60.6 g and 75.5 g/100 mL at 0° and 20°C , respectively—solubility increasing approximately 16 to 18 g/100 mL for every 20°C increase in temperature.

Thermochemical Properties

$\Delta H_f^\circ(\text{s})$	−64.73 kcal/mol
$\Delta G_f^\circ(\text{s})$	−41.9 kcal/mol
S°	27 cal/degree mol
C_p	23 cal/degree mol

Preparation

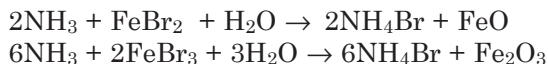
Ammonium bromide is prepared by treating excess ammonia with bromine:



It may be also prepared by the reaction of ammonia and hydrobromic acid:

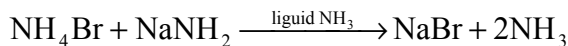


NH_4Br is also made by the reaction of ammonia with ferrous and ferric bromide, which may be obtained by passing aqueous bromine solution over iron filings.

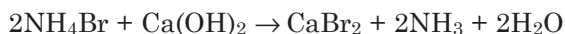


Reactions

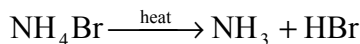
Ammonium bromide exhibits acid reaction in aqueous solution; acts as an excellent acid in liquid NH_3 , undergoing neutralization reactions:



Contact with metal surfaces produces bromides of the metals; similarly reactions with metal hydroxide bases yield corresponding bromides:



Ammonium bromide decomposes to ammonia and hydrogen bromide when heated at elevated temperatures:



Chemical Analysis

Elemental composition: Br 81.58%, H 4.12%, N 14.30%

Mixed with NaOH solution and distilled; distillate analyzed for ammonia by titration, colorimetry, or electrode method (see Ammonia and Ammonium chloride). Bromide portion of NH_4Br in aqueous solution may be analyzed by ion chromatography, or by the colorimetry method in which red to violet color is produced upon treatment with chloramine-T, and phenol red at pH 4.5. The colorimetry test for bromide is subject to interference from oxidizing and reducing agents, chloride, and bicarbonate. NH_4Br may then be determined stoichiometrically.

AMMONIUM CARBAMATE

[1111-78-0]

Formula: $\text{NH}_2\text{COONH}_4$; MW 78.07;

Synonyms: ammonium aminoformate; ammonium carbonate anhydride

Uses

Ammonium carbamate is used as an ammoniating agent. It occurs as a mixed salt with ammonium bicarbonate and carbonate.

Physical Properties

Colorless rhombic crystal; odor of ammonia; sublimes at 60°C ; very soluble in cold water; decomposes in hot water; slightly soluble in alcohol; insoluble in acetone.

Preparation

Ammonium carbamate is prepared from dry ice and liquid ammonia:



Reactions

Decomposes on heating to ammonia and carbon dioxide; in contact with air at ambient temperatures, it loses ammonia, forming ammonium carbonate. In

solution, it is partly hydrolyzed to carbonate.



The carbamate is decomposed by acids and their salts.

AMMONIUM CARBONATE

[506–87–6]

Formula: $(\text{NH}_4)_2\text{CO}_3 \cdot \text{H}_2\text{O}$; MW 114.10; not available in pure form; crystalline products consist of double salts of ammonium carbonate, ammonium bicarbonate, and ammonium carbamate.

Synonyms: salt of hartshorn; sal volatile

Uses

Applications of ammonium carbonate are similar to those of ammonium bicarbonate. It is used in baking powder; in fire extinguishers; as mordant in dyeing; for washing and defatting wools; in tanning; in manufacture of rubber products; as a “smelling salt”; as a source of ammonia, and as an expectorant.

Physical Properties

Colorless or translucent hard crystalline mass or white cubic crystals or powder; sharp taste; odor of ammonia; decomposes at 58°C; slow decomposition at ambient temperatures; readily dissolves in cold water; decomposes in hot water; insoluble in liquid ammonia, alcohol and carbon disulfide.

Preparation

Ammonium carbonate is obtained by passing carbon dioxide into aqueous ammonia solution in a column or tower. Ammonia, carbon dioxide and water vapor are distilled and the vapors condensed into a solid crystalline mass. It also may be prepared by subliming a mixture of ammonium sulfate and calcium carbonate.

Reactions

Ammonium carbonate slowly decomposes on exposure to air, or rapidly breaks down on heating to ammonia, CO_2 , and water; liberates CO_2 on treatment with dilute mineral acids. It reacts with metals forming their carbonates. Reaction with hydriodic acid produces ammonium iodide; and forms ammonium oxalate with oxalic acid.

AMMONIUM CHLORIDE

[12125–02–9]

Formula: NH_4Cl ; MW 53.49

Synonym: Sal ammoniac

Occurrence and Uses

Ammonium chloride occurs in nature in crevices near volcanoes. Also, it is found in smoke when burning dry camel or donkey dung as fuel. Important applications of this compound include the manufacture of dry cells for batteries; as a metal cleaner in soldering; as a flux in tin coating and galvanizing; in fertilizers; in pharmaceutical applications as a diuretic, or diaphoretic expectorant; and as an analytical standard in ammonia analysis. Also, it is used in freezing mixtures; washing powders; lustering cotton; in safety explosives and in dyeing and tanning.

Physical Properties

Colorless cubic crystals or white granular powder; saline taste; odorless; hygroscopic; does not melt but sublimes on heating at 340°C; vapor pressure 48.75 torr at 250°C and 251.2 torr at 300°C; density 1.5274 g/cm³ at 25°C; refractive index 1.642; readily dissolves in water, solubility: 229 g and 271 g/L solution at 0°C and 20°C, respectively; solubility lowered by alkali metal chlorides and HCl; dissolution lowers the temperature of the solution; sparingly soluble in alcohols (6 g/L at 19°C) and soluble in liquid NH₃; insoluble in acetone and ether.

Thermochemical Properties

$\Delta H^\circ f(s)$	-75.15 kcal/mol
$\Delta H^\circ f(s)$ [NH ₃ (g) + HCl(g)]	-41.9 kcal/mol
$\Delta G^\circ f(s)$	-48.51 kcal/mol
S°	22.6 cal/degree mol
C _p	20.1 cal/degree mol
$\Delta H^\circ_{\text{subl}}$ (1 atm)	39.6 kcal/mol

Manufacture

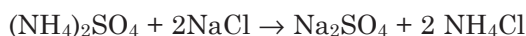
Ammonium chloride is produced as a by-product in the Solvay process for manufacture of sodium carbonate:



NaHCO₃ precipitate is filtered out of solution while NH₄Cl is obtained by crystallization followed by washing and drying. Ammonium chloride also is produced from spent calcium chloride liquor obtained in ammonia-soda process:

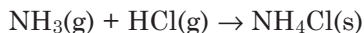


It also is made by heating a mixture of slight excess of NaCl solution with ammonium sulfate. The filtrate containing NH₄Cl is concentrated and cooled. NH₄Cl crystallizes:



It is produced by direct neutralization reaction of NH₃ and HCl combined as

gaseous mixtures.



Reactions

NH_4Cl is acidic in aqueous solution: the pH of 1%, 3%, and 10% solution at 25°C are 5.5, 5.1 and 5.0, respectively. (Merck 1996. *The Merck Index*, 12th ed. Rahway, NJ: Merck & Co.) It loses ammonia and becomes more acidic on prolonged exposure or storage. It reacts with iron, copper, nickel and other metals and some of their alloys such as bronze and brass. It reacts with alkalis forming NH_3 .

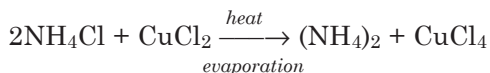


Ammonium chloride decomposes to ammonia and HCl when heated. The vapor resulting from sublimation consists of equal volume of NH_3 and HCl, and does not consist of molecular NH_4Cl . (Young, R. D. 1976. Ammonium Compounds. In *Kirk-Othmer Encyclopedia of Chemical Technology*, 3rd. ed. Vol. 2, p. 521. New York: Wiley Interscience.)

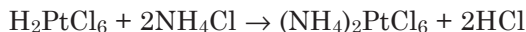
Reacts with formaldehyde (neutralized with NaOH) forming hexamethylenetetramine and HCl.



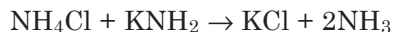
Reaction with copper(II) chloride at 2:1 ratio produces yellow orthorhombic crystals of cupric ammonium chloride, which reacts with water to form blue dihydrate crystal, ammonium tetrachlorodiaquocuprate(II):



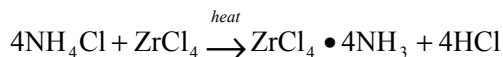
A similar complex formation occurs with mercuric chloride, zinc chloride, osmium chloride and platinum (II) and (VI) chlorides, forming mercuric ammonium chloride, $(\text{NH}_4)_2 \cdot \text{HgCl}_4$, zinc ammonium chloride $(\text{NH}_4)_3\text{ZnCl}_4$ or $\text{ZnCl}_2 \cdot 3\text{NH}_4\text{Cl}$, osmium ammonium chloride, $(\text{NH}_4)_2\text{OsCl}_6$, platinum ammonium chloride, $(\text{NH}_4)_2\text{PtCl}_4$ and platinic ammonium chloride $(\text{NH}_4)_2\text{PtCl}_6$, respectively. Similarly, it reacts with palladium chloride to form ammonium chloropalladate, $(\text{NH}_4)_2\text{PdCl}_4$. It precipitates out ammonium platinichloride from solution of chloroplatinic acid (Archibald, E. H. 1920. *J. Chem. Soc.*, 117, 1105):



Neutralization reaction occurs with amide, forming chloride salt and ammonia:



Heating with zirconium chloride gives a tetraamine adduct:



Chemical Analysis

Elemental composition: Cl 66.28%, H 7.54%, N 26.18%

Ammonium chloride is analyzed by treatment with formaldehyde (neutralized with NaOH) and the product HCl formed is analyzed by titration using an acid-base color indicator such as phenolphthalein. Alternatively, it may be mixed with caustic soda solution and distilled. The distillate may be analyzed for NH_3 by titration with H_2SO_4 ; or by colorimetric Nesslerization; or with an ammonia-selective electrode (APHA, AWWA, WEF. 1995. *Standard Methods for the Examination of Water and Wastewater*. 19th ed. Washington, DC, American Public Health Association). The presence of ammonia or any other ammonium compound would interfere in the test. The moisture content in NH_4Cl may be determined by Karl–Fischer method.

AMMONIUM CYANIDE

[12211–52–8]

Formula: NH_4CN ; MW 44.056

Uses

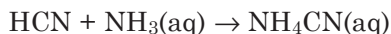
NH_4CN is used in organic synthesis. Unstable, it is not shipped or sold commercially.

Physical Properties

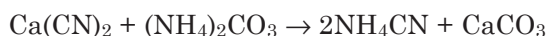
Colorless crystalline solid; cubic crystal; unstable; density 1.02 g/cm³; decomposes at 36°C; sublimes at 40°C; very soluble in cold water and alcohol; decomposes in hot water.

Preparation

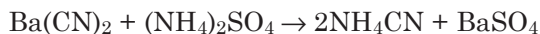
Ammonium cyanide is prepared in solution by bubbling hydrogen cyanide into aqueous ammonia at low temperature:



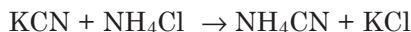
It may be prepared in solution by the reaction of calcium cyanide and ammonium carbonate:



or barium cyanide and ammonium sulfate:



In dry state, NH_4CN is made by heating a mixture of potassium cyanide or potassium ferrocyanide with ammonium chloride and condensing the vapors into ammonium cyanide crystals:



Reactions

Ammonium cyanide decomposes to ammonia and hydrogen cyanide; often forming black polymer of HCN:



It undergoes double decomposition reactions in solution with a number of metal salts. It reacts with glyoxal producing glycine (aminoacetic acid)



Reactions with ketones yield aminonitriles:



Analysis

Elemental composition: H 9.15%, C 27.23%, N 63.55%.

NH_4CN may be analyzed by heating the salt and trapping the decomposed products HCN and ammonia in water at low temperatures. The aqueous solution is analyzed for cyanide ion by silver nitrate titrimetric method or an ion-selective electrode method; and ammonia is measured by titration or electrode technique (Patnaik, P. 1997. *Handbook of Environmental Analysis*, Boca Raton, FL: Lewis Publishers).

Toxicity

The solid or its solution is highly toxic. Ingestion can cause death. Exposure to the solid can be harmful as it decomposes to highly toxic hydrogen cyanide and ammonia.

AMMONIUM DICHROMATE

[7789-09-5]

Formula: $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$; MW 252.10

Synonym: ammonium bichromate

Uses

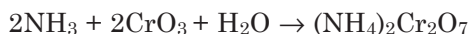
Ammonium dichromate is used in pyrotechnics; in photoengraving and lithography; as a source of pure nitrogen in the laboratory; and as a catalyst.

Physical Properties

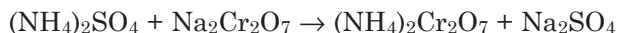
Bright orange-red monoclinic crystals; odorless; hygroscopic; decomposes at 180°C; density 2.115 g/cm³ at 25°C; readily dissolves in water (26.67 g/100 g at 20°C).

Preparation

(NH₄)₂Cr₂O₇ may be prepared by the reaction of ammonia gas with chromic acid:



or ammonium sulfate with sodium dichromate:

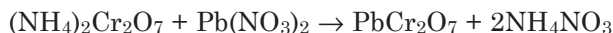


Reactions

(NH₄)₂Cr₂O₇ decomposes at 180°C. On further heating to 225° C it begins to swell and dissociates exothermically, liberating nitrogen and water vapor, leaving behind a residue of chromium(III) oxide:



As an acid salt, its solution is acidic (pH 3.45 and 3.95 for a 10% and 1% solution, respectively). It undergoes acid reactions. Also, it undergoes double decomposition reactions, forming metal dichromates:



As an oxidizing agent, it undergoes oxidation-reduction reactions with reducing agents at ambient and elevated temperatures.

Hazard

Ammonium dichromate is an irritant to skin. Inhalation of dusts can cause pulmonary irritation, perforation of the nasal septum and “chrome sores.” Ingestion can cause ulceration. It is also a flammable salt.

AMMONIUM FLUORIDE

[12125–01–8]

Formula: NH₄F; MW 31.04

Synonyms: neutral ammonium fluoride; normal ammonium fluoride

Uses

NH₄F is used for etching glass; for preserving wood; as a mothproofing agent; in printing and dyeing textiles; and as an antiseptic in brewery

Physical Properties

White, deliquescent, crystalline solid; occurs in various forms, as granular powder (commercial products), needles or leaflets, or hexagonal prism (formed on sublimation and condensation); density 1.009 g/cm³ at 25°C; decomposes on heating; highly soluble in cold water (100g/100g at 0°C); decomposes in hot water; slightly soluble in alcohol, insoluble in liquid ammonia

Thermochemical Properties

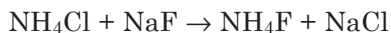
$\Delta H^\circ f$	-110.89 kcal/mol
$\Delta G^\circ f$	-83.36 kcal/mol
S°	17.20 cal/degree mol
C_p	15.60 cal/degree mol

Preparation

NH₄F is made by passing ammonia gas through a 40% aqueous solution of hydrofluoric acid (ice-cooled):



Alternatively, it may be prepared by heating ammonium chloride with excess sodium fluoride. Ammonium fluoride is obtained by sublimation.



Also, it may be prepared by mixing an equimolar amount of aqueous ammonia and ammonium bifluoride.

Reactions

Decomposes on heating to ammonia and hydrogen fluoride; also decomposes in hot water producing ammonia and ammonium bifluoride:



The solution is acidic; it reacts with weak bases forming double salts; i.e., ammonium hexafluoroaluminate, (NH₄)₃AlF₆; ammonium hexafluorophosphate, NH₄PF₆; ammonium hexafluorosilicate, (NH₄)₂SiF₆; ammonium hexafluorogallate, (NH₄)₃GaF₆:



Chemical Analysis

Elemental composition: F 51.30%, H 10.88%, N 37.82%. A measured amount is dissolved in water and the aqueous solution diluted appropriately and analyzed for fluoride by fluoride ion-selective electrode, or by ion chromatography. Ammonium ion (or liberated ammonia) is analyzed by titration or by ammonium ion-specific electrode (see Ammonia).

Toxicity

NH₄F is a highly toxic substance; ingestion can cause nausea, vomiting, abdominal pain, tremor, hemorrhage, muscular weakness, convulsions and vascular collapse. Ingestion of large quantity can cause death. Chronic effects include mottling of enamel, osteoclerosis and calcification in ligaments.

AMMONIUM FORMATE

[540–69–2]

Formula: HCOONH₄; MW 63.06;

Synonym: formic acid ammonium salt

Uses

Ammonium formate is used in chemical analysis to separate base metals from noble metal salts.

Physical Properties

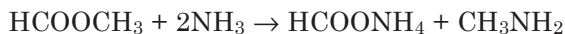
White monoclinic deliquescent crystals or granules; density 1.280 g/cm³; melts at 116°C; highly soluble in water (102 g/100 g at 0°C), solubility rapidly increasing with temperature (i.e., 531 g/100 g at 80°C); soluble in liquid ammonia, alcohol and ether.

Preparation

NH₄COOH is prepared by the reaction of ammonia with formic acid:



or from methyl formate and ammonia:

**Reactions**

Thermal dissociation produces ammonia, carbon dioxide, and water; reacts with metal salts forming their formates; oxidized by strong oxidants forming carbon dioxide, water, and oxides of nitrogen.

AMMONIUM HYDROSULFIDE

[12124-99-1]

Formula: NH_4HS ; MW 51.113

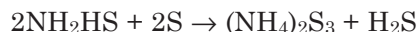
Synonyms: ammonium sulfhydrate, ammonium bisulfide, ammonium hydrogen sulfide

UsesAqueous solutions of NH_4HS are used in various commercial applications including textile manufacture.**Physical Properties**White tetragonal or orthorhombic crystal; density 1.17g/cm^3 ; refractive index 1.74; unstable, sublimes readily at ordinary temperatures; vapor pressure 748 torr at 32°C ; highly soluble in water, alcohol, liquid ammonia and liquid hydrogen sulfide; insoluble in benzene, hexane and ether.**Thermochemical Properties**

ΔH°_f	-37.5 kcal/mol
ΔG°_f	-12.1 kcal/mol
S°	23.3 cal/degree mol

Preparation NH_4HS is prepared by the reaction of an equimolar amount of ammonia and hydrogen sulfide:**Reactions**

When heated, the hydrosulfide dissociates into ammonia and hydrogen sulfide; addition of sulfur produces ammonium sulfide:



AMMONIUM MOLYBDATE

[27546-07-2]

Formula: $(\text{NH}_4)_2\text{MoO}_4$; MW 196.01Ammonium ion forms isopolymolybdates, such as di-, tri-, or heptamolybdates with the molybdate anion. Only the dimolybdate, $(\text{NH}_4)_2\text{Mo}_2\text{O}_7$, and ammonium heptamolybdate $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ [12027-67-7], have commercial applications.**Uses**

Ammonium molybdates are used to prepare high purity grade molybdenum metal powder, sheet, or wire; for colorimetric analysis of phosphates and arse-

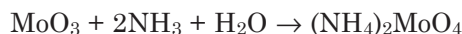
nates; for decorating ceramics; and as catalysts.

Physical Properties

Colorless, monoclinic crystal; density 2.276 g/cm³; decomposes on heating; soluble in water (decomposes); also soluble in acid; insoluble in alcohol and liquid ammonia.

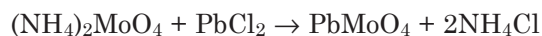
Preparation

Ammonium molybdate is prepared by treating molybdenum oxide with excess ammonia in an aqueous solution. The crystals are obtained after evaporation of water.



Reactions

Decomposes on heating or on treatment with alkalis; reacts with lead chloride and other metal salts to form their metal molybdates:



Reacts with phosphates or arsenates to form ammonium phosphomolybdate $(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3$, or ammonium arsenomolybdate, $(\text{NH}_4)_3\text{AsO}_4 \cdot 12\text{MoO}_3$.

Chemical Analysis

Elemental composition: H 4.11%, Mo 48.94%, N 14.29%; O 32.65.

$(\text{NH}_4)_2\text{MoO}_4$ is digested with nitric acid and the molybdenum metal is analyzed by atomic absorption or emission spectrophotometry. It is dissociated to ammonia, which may be measured by titration or by an ion-specific electrode technique (see Ammonia). Ammonium molybdate reacts under acid conditions with dilute orthophosphate solution to form molybdophosphoric acid which, in the presence of vanadium, forms yellow vanadomolybdophosphoric acid; the intensity of the yellow color may be measured by a spectrophotometer at 400 to 490 nm and is proportional to the trace amount of ammonium molybdate.

AMMONIUM NITRATE

[6484–52–2]

Formula: NH_4NO_3 ; MW 80.043

Uses

The ammonium salt produced or consumed in largest amounts is ammonium nitrate. It is used widely as a fertilizer, and is the leading nitrogen fertilizer in the world. An advantage of this compound over other ammonium fertilizers is that it provides both nitrate and ammonia to soil without changing the pH. Also, it is used as a mixed fertilizer with other compounds, such as calcium phosphate, or calcium carbonate. It also is used as an explosive for

blasting, or as an ingredient of various mines, or in highway construction. The salt itself, or in combination with fuel oil, powdered aluminum, or carbonaceous matter, is a high explosive. Its blend with trinitrotoluene, known as Amatol, is a military explosive.

Other uses of ammonium nitrate are in the manufacture of nitrous oxide, an anesthetic, and as a component of freezing mixtures.

Physical Properties

White crystalline solid; occurs in five different crystallographic modifications as follows:

- (i) tetragonal form below -18°C
- (ii) rhombic form between -18 to 32.1°C
- (iii) rhombic form between 32.1 to 84.2°C
- (iv) tetragonal form between 84.2 to 125.2°C
- (v) cubic form between 125.2 to 169.6°C ;

density 1.725 g/m^3 at 20°C ; highly hygroscopic; the finely divided powder cakes to a hard mass on storage; melts at 169.6°C ; extremely soluble in water; its solubility in 100 g water is as follows:

0°C	118 g
20°C	150 g
40°C	297 g
60°C	410 g
80°C	576 g

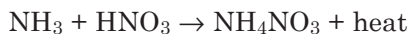
Dissolution is endothermic, solution becomes cold (and hence its application in freezing bath); elevates the boiling point of water by 1° , 7.5° , 28.5° and 70°C at 10, 40, 80 and 95% (w/w) concentrations, respectively; vapor pressure of saturated solution, 11.2 torr at 20°C .

Thermochemical Properties

$\Delta H^{\circ}f$ (solid)	-87.37 kcal/mol
$\Delta H^{\circ}f$ (aq)	-81.23 kcal/mol
$\Delta G^{\circ}f$ (solid)	-43.98 kcal/mol
$\Delta G^{\circ}f$ (aq)	-45.58 kcal/mol
S° (solid)	$36.11\text{ cal/degree mol}$
S° (aq)	$62.10\text{ cal/degree mol}$
C_p (solid)	$33.3\text{ cal/degree mol}$

Manufacture

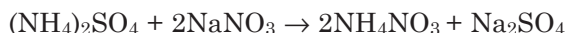
NH_4NO_3 is made by the neutralization reaction of ammonia with nitric acid:



The reaction is carried out in aqueous phase using a slight excess of nitric acid. The heat of reaction is utilized to evaporate the water. Also, evaporation may be carried out under vacuum. Alternatively, solid ammonium nitrate is obtained by crystallization from a concentrated solution. The particle size of the dry product may be controlled by vacuum crystallization, granulation or

other processes. (Young, R.D. 1978. Ammonium Compounds. In *Kirk-Othmer Encyclopedia of Chemical Technology*, 3rd ed., Vol. 2, pp. 525–532. New York: Wiley Interscience.) The solid powder should be protected from moisture to minimize caking.

Ammonium nitrate alternatively may be prepared by double decomposition reactions of ammonium salt with a nitrate salt; e.g., ammonium sulfate and sodium nitrate:

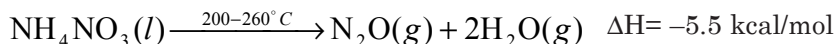


Reactions

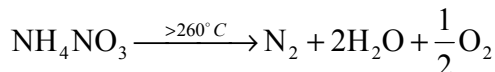
Ammonium nitrate volatilizes reversibly with dissociation at moderate temperatures:



Thermal decomposition occurs at 170°C producing nitrous oxide and water:

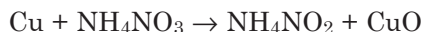


N₂O evolves smoothly; however, above 250°C or if the solid is strongly shocked, violent decomposition occurs:



Aqueous solutions of ammonium nitrate undergo a double decomposition reaction with metal salts. NH₄NO₃ acts as an oxidizing agent in aqueous solutions and is reduced by various metals at ambient temperatures.

Spongy copper slowly reduces it to ammonium nitrite in the absence of air; however, no reaction occurs with copper wire or gauge. (Basset, H. and R. G. Durrant. 1922. *J. Chem. Soc.*, 121, 2631):



Chemical Analysis

Ammonium nitrate dissociates in aqueous solution to NH₄⁺ and NO₃⁻ ions. The former may be measured by ammonium ion-selective electrode and the latter by nitrate ion-selective electrode. The solid may be heated carefully at low temperature (around 90°C) and the evolved ammonia and nitric acid vapors are absorbed in water and measured by selective ion electrodes, respectively.

Hazard

Heating ammonium nitrate can present a severe explosion hazard. When heated above 210°C, its decomposition is exothermic, producing nitrous oxide and water vapor. In closed confinement, heating the molten mass can cause a pressure build-up. Above 300°C, there is rapid evolution of nitrogen, water

vapor and oxygen—two mols solid producing seven mols of gaseous products. This can cause a dangerous explosion. In the presence of readily oxidizable substances, such as fuel oil soaked into the pores of the solid or finely divided metal, the ignition is self-sustained—occurring at lower temperatures, and the explosivity is enhanced. Also, it can explode dangerously in a fire. At ordinary temperatures, the compound is stable and safe to handle. Calcium carbonate, phosphate or other substances are mixed with fertilizer grade ammonium nitrate to reduce its explosivity. There are many cases of loss of human lives from ammonium nitrate fire or explosion.

AMMONIUM PHOSPHATE, DIBASIC

[7783–28–0]

Formula: $(\text{NH}_4)_2\text{HPO}_4$; MW 132.07;

Synonyms: diammonium hydrogen phosphate; secondary ammonium phosphate

Uses

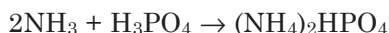
Dibasic ammonium phosphate is used as a fertilizer; as a fire extinguisher; a flame retardant for plywood, papers, and fabrics; to prevent afterglow in matches; in purifying sugar; as a flux for soldering tin, copper, zinc and brass; and to control precipitation of alkali-soluble or acid-insoluble colloidal dyes on wool.

Physical Properties

Colorless monoclinic crystal; saline taste; refractive index 1.52; density 1.619 g/cm³; melts at 155°C (decomposes); very soluble in water (57 g/100 g at 10°C and 106.7g/100g at 70°C, respectively); insoluble in alcohol, acetone, and liquid ammonia.

Preparation

$(\text{NH}_4)_2\text{HPO}_4$ is made by reacting ammonia with phosphoric acid:



Reactions

Heating at 70°C results in decomposition to monoammonium phosphate and ammonia:



A boiling, dilute solution of diammonium phosphate evolves ammonia (the pH of the solution decreases), which also occurs slowly at ambient temperatures. The solid and its solution create an ammonia vapor pressure. Reactions with mineral acids produce the corresponding ammonium salts.